

Simple Test Guidelines for Screening Oilspill Sorbents for Toxicity

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Abstract

A variety of commercial sorbents available loose, as sheets, or in socks were obtained in order to generate simple test guidelines for screening sorbent toxicity. Three test species were evaluated for suitability. Threespine stickleback acute lethality tests (saltwater) were not as sensitive an indicator of sorbent toxicity as the rainbow trout acute lethality tests (freshwater) and sea urchin fertilization assays (saltwater). Sea urchin fertilization assays and rainbow trout acute lethality tests were recommended for future testing. A number of handling issues were then addressed. The toxicity of test solutions prepared from sorbents soaked for 1 and 24 hours was compared to determine the optimal time for solution preparation. Sorbents should be soaked for 24 hours prior to testing, then removed, and squeezed to extract water that is returned to the tank before test organisms are exposed. Special handling concerns were also addressed. Sheet-type sorbents should be diced into 1 cm cubes prior to soaking. Three means of handling sock-type sorbents were evaluated. Solutions were prepared from the intact sorbent, the loose product filtered through a dip net, and the loose product filtered through the sock material. For sock-type sorbents, solutions should be prepared from the intact sorbent, and from the loose product filtered through a dip net (approx. 0.5 mm mesh size).

1.0 Introduction

The Emergencies Science Division of Environment Canada maintains a continuing program to measure the toxicity of substances that are spilled as well as the toxicity of spill treating agents. This information is used to evaluate alternative countermeasures as well as to select countermeasures likely to cause as little environmental damage as possible.

Sorbents are materials which are used to absorb or adsorb spilled oil and other hazardous materials. They vary widely in composition (natural, synthetic, or a mixture) and packaging (e.g. loose, sheets, socks). In addition, sorbent materials may be treated with oleophilic and hydrophobic compounds to improve performance (Cooper *et al.*, 1994).

Sorbents can be used in large quantities during spills of oils or other hazardous materials. The efficacy of various sorbents has been assessed in the past (S.L. Ross Environmental Research Limited, 1991; Cooper *et al.*, 1994), but potential toxicity has not been considered.

To address this information gap, the Emergencies Science Division of Environment Canada embarked on a program to develop a standard test method suitable for evaluating the toxicity of common sorbent materials. The testing of sorbents poses three main handling problems:

- ▶ sorbents are generally of low solubility or insoluble in water,
- ▶ some sorbents absorb water, and
- ▶ sorbents may be packed in layers in a sock or sold as sheets, which present problems with exposure to test organisms.

The work described in this paper was performed in two phases. In the Species Selection Phase, a variety of sorbents were obtained to determine appropriate test species and to gain experience and knowledge with respect to how to handle the range of sorbent types available.

Several questions arose, which were addressed in the Material Handling Phase. These questions included:

- ▶ what is the optimum soaking time for screening sorbents for toxicity
- ▶ does the toxicity of sorbents change if tested with or separate from sock enclosure material
- ▶ does dicing sheet material alter the toxicity, if so, what is the optimum size

In order to generate broadly applicable guidelines, a range of natural and synthetic products were obtained from the Emergencies Engineering Division of Environment Canada as well as directly from sorbent manufacturers. The general composition of the products is stated, but the products are not identified by trade name. Several of the sorbents tested are not currently commercially available.

2.0 Methods

2.1 Sorbents

During the Species Selection Phase, five loose or sheet-type sorbent samples were obtained from the Emergencies Engineering Division (EED), Environmental Technology Centre in Ottawa. These products are identified as A through E, and brief composition descriptions given in Table 1.

During the Material Handling Phase, six sorbents with different trade names from those used in the first phase of testing were obtained, three natural products (F, G, K) and three synthetic products (H, I, J). One sheet-type product (L) was also obtained. Brief composition descriptions are given in Table 1.

2.2 Toxicity Testing of Sorbents

General information on the toxicity tests performed in the Species Selection and in the Material Handling Phases is given below. Specific information on experimental variables (e.g. sorbent handling, soaking time, sorbent removal) is given in Sections 2.3 and 2.4.

Table 1 Description of Sorbents Used in Test Guideline Development

Product	Description
A	Loose, grey, egg carton-like particles
B	Sponge-like sheets of very low density
C	Loose, black, rice-shaped particles
D	Loose, looks like peat moss
E	Loose laundry detergent-sized particles
F	Loose peat moss product
G	Loose cotton cellulose
H	Loose fibreglass
I	Polypropylene in Sock
J	Ground rubber tire in Sock
K	Wool/Cotton in Sock
L	Sheet (largely polypropylene)

2.2.1 Rainbow Trout Acute Lethality

The appropriate volume of control/dilution water (soft, dechlorinated municipal) was added to the test vessel. Test concentrations were made by weighing the required amount of product, and adding it to the appropriate tanks. The product was soaked, removed, and the test solutions were then pre-aerated for 30 minutes at 6.5 ± 1 mL air/minute/L solution. After the pre-aeration period the test organisms were introduced and the tests begun. Tests were conducted according to EPS 1/RM/9 (Environment Canada, 1990a). Test duration was 96 hours. Data was analyzed for LC50 value using the method of Stephan (1977) in the Species Selection Phase and using Toxstat Version 3.5 statistical software in the Material Handling Phase. The LC50 is an estimate of the concentration in which half of the test organisms die. It usually has a time value (ie. 96h LC50). The LC50 is quoted with 95% confidence limits.

2.2.2 Sea Urchin Fertilization Inhibition

Lytechinus pictus was received from California and held at the lab at a temperature of $13 \pm 2^\circ\text{C}$ and a salinity of 30 ± 2 ppt. The sorbent was added to glass containers partially filled with the appropriate volume of natural saltwater from a clean source (0.45 to $0.8 \mu\text{m}$ filtered). The appropriate weight of sample was mixed with the seawater, soaked, and removed. The initial chemistry readings were taken and recorded (temperature, dissolved oxygen, pH, and salinity). Test procedure

followed EPS 1/RM/27 (Environment Canada, 1992). Eggs were scored within 3 days of testing. Test volume was 10 mL and test duration was 20 minutes. Sperm to egg ratio was fixed at 20,000:1.

2.2.3 Threespine Stickleback Acute Lethality

Threespine stickleback were collected by beach seine and acclimated to the test conditions (10°C, and a salinity of 30 ± 2 ppt). The appropriate volume of natural seawater (salinity 30 ± 2 ppt) was added to the test vessel. To prepare the test concentrations, the required amount of product was weighed, added to the appropriate tanks, soaked, and removed. The test solutions were pre-aerated for 30 minutes at 7.5 mL air/minute/L solution. After the pre-aeration period the test organisms were introduced and the tests begun. Tests were conducted according to the method EPS 1/RM/10 (Environment Canada, 1990b). Test duration was 96 hours. Data were analyzed for 96 hour LC50 using the method of Stephan (1977).

2.3 Species Selection Phase

The toxicity of five sorbents (A to E) to three aquatic organisms was evaluated using the rainbow trout acute lethality (freshwater), threespine stickleback acute lethality (seawater) and sea urchin fertilization inhibition tests (seawater).

Prior to solution preparation, the sheet-type sorbent (Product B) was diced into 2.5 cm cubes. The maximum sorbent loading was 40 g/L. All products were soaked for 24 hours. At the end of the 24 hour soaking period, the loose product was removed from solution using a clean dip net (approximately 0.5 mm mesh size). Any water which had soaked into the product was squeezed back into the test solution.

2.4 Material Handling Phase

2.4.1 Determination of Optimal Soaking Time

Three loose sorbent products (F, G, H), and three cased sorbent products (I, J, K) were soaked for 1 and 24 hours. The maximum sorbent loading was 10 g/L. Prior to introducing the test species, the loose sorbents were removed from the test solution using a small hand-held dip net (approximately 0.5 mm mesh size). In general, the material removed was squeezed to remove most of the liquid, which was returned to the test container. The sorbent socks were simply lifted out and squeezed to remove most of the liquid, which was returned to the test container. The rainbow trout acute lethality test was performed on the resultant solutions.

2.4.2 Determination of Sheet-type Sorbent Handling & Soaking Time

The sheet-type Product L was handled two ways (diced into 1 cm cubes or left intact in large chunks), and solutions prepared by soaking the sorbent for 1 and 24 hours. The maximum sorbent loading was 10 g/L. Prior to introducing the test species, the diced sorbent material was removed from the solution using a fish net, and the intact sheet material simply removed by hand. The material removed was squeezed to remove most of the liquid, which was returned to the test container. A 96 hour rainbow trout acute lethality test was performed on the resultant solutions.

2.4.3 Determination of Sock-type Sorbent Handling

The toxicity of the solutions generated below from several sock-type sorbent samples (I, J, K) was assessed using the Rainbow Trout Acute Lethality Test and the Sea Urchin Fertilization Inhibition Assay. The maximum sorbent loading was 10 g/L. Where necessary, the sock-type sorbents were cut into appropriate weights and sock sizes reconfigured to fit into the test vessels. Care was taken not to introduce foreign materials during this process (i.e., only materials from the original sock were used if socks were re-sewn).

Sorbent Minus Sock: The sorbent was removed from the sock, and soaked for 24 hours. The loose sorbent was removed from solution using a dip net or picked out, except for Product I, which was left in the solution during testing with rainbow trout. Product I was tested prior to the decision to dip net or pick out loose sorbents prior to test organism introduction.

Sorbent Solution Filtered Through the Sock: The sorbent was removed from the sock, and soaked for 24 hours. The loose sorbent was removed from solution by filtering through a piece of the original sock prior to testing.

Sorbent Tested Intact: The intact sorbent sock was soaked for 24 hours, removed, and the resultant solution tested.

Additional Tests: In addition to the above tests, several additional studies were performed. Product J was tested loose with the material left in during a Rainbow Trout Acute Lethality Test to look at the effects of suspended material on the LC50. The remaining tests were performed using the Sea Urchin Fertilization Inhibition Assay only. Product I was tested as sock casing material only, after 24 hours soaking. The first experiment tested a piece 10 cm x 10 cm (0.77g) and another piece 20 cm x 20 cm (3.48 g) in 1 litre of seawater. These sizes were chosen since a piece of sock 20 x 20 was required to wrap 10 g of sorbent material. The test was repeated with 3 sizes, 10 x 10 (0.77 g), 3 x 3 (0.07 g) and 1 x 1 cm (0.01 g). Product J was tested loose with the material left in at test initiation and loose filtered through a 0.45 μ m filter.

3.0 Results

3.1 Species Selection

Overall mortality in the controls for the rainbow trout and threespine stickleback tests was 0%. Overall fertilization in the sea urchin controls was 95%. All tests were valid.

The threespine stickleback acute lethality tests (seawater) were not as sensitive an indicator of sorbent toxicity as the rainbow trout acute lethality tests (freshwater) and sea urchin fertilization assays (seawater)(Table 2). Threespine stickleback were therefore not used in the Material Handling Phase.

Table 2 Toxicity Test Results of Sorbents to Various Organisms

PRODUCT	20-min IC50 (Sea Urchin) g/L	96-hr LC50 (Rainbow Trout) g/L	96-hr LC50 (Threespine stickleback) g/L
B	1.42 (1.38 - 1.45)	1.76 (1.25 - 2.50)	5.00 (2.50 - 10.00)
D	2.87 (1.74 - 4.23)	4.32 (3.24 - 5.77)	14.20 (10.00-20.00)
C	2.90 (2.46 - 3.43)	0.150 (0.094 - 0.375)	>40
E	3.55 (2.50 - 5.54)	>40	>40
A	5.80 (4.86 - 6.94)	>40	>40

The sheet-type Product B had been diced into small cubes to maximize surface area, and this was a very time-intensive task. Handling of sheet-type sorbents was chosen as an issue for the final method development phase.

A maximum of 10 g of sorbent was chosen as an upper limit for future testing. For low density products, higher sorbent concentrations would take up the whole volume of water in the test tank. In addition, if the 96 hour LC50 is greater than 10 g/L, the product would be considered practically non-toxic (Sprague, 1973).

3.2 Material Handling

Overall mortality in the rainbow trout controls was 0.7%. Overall fertilization in the sea urchin controls was 87.2%. All tests were valid.

For four of the six sorbents tested, there was very little difference in the 96 hour LC50s for rainbow trout exposed to test solutions prepared by 1 and 24 hours of soaking (Table 3). However, Product K was definitely more toxic to rainbow trout after 24 hours of soaking. For Product J, the 1 hour soak caused 20% mortality at 10,000 mg/L, and the 24 hour soak caused 90% mortality at 10,000 mg/L. The soaking time was therefore standardized at 24 hours for the remainder of the screening tests.

Table 3 Effect of Sorbent Soaking Time on Toxicity using the Rainbow Trout
96 hour Acute Lethality Test

PRODUCT	Rainbow Trout 96 hour LC50 (95% Confidence Limits) g/L	
	1 Hour Soak	24 Hour Soak
F	>10	>10
G	3.00 (2.43 - 3.57)	3.19 (2.66 - 3.72)
H	>10	>10
I	>10	>10
J	>10	9.92 (7.19 - 46.0)
K	>10	7.13 (6.43 - 7.82)

Handling method (intact and diced) and soaking time (1 and 24 hours) did not affect toxicity test results for the sheet-type (Product L) sorbent. All test solutions were not toxic, with rainbow trout 96 hour LC50's of >10,000 mg/L.

The handling method (intact, loose filtered through net, loose filtered through sock) definitely had an impact on the measured toxicity of the sock-type sorbents, and this effect was not consistent between sorbent types (Figures 1 & 2). Two of the products (J, K) were less toxic when tested intact, and one product was more toxic (I) when tested intact.

It appears that Product J had a toxic water soluble fraction. The loose Product J left in throughout the testing had a rainbow trout 96 hour LC50 of 0.054 (0.017 - 0.092) g/L while the product filtered through the sock material had a similar LC50 of 0.059 (0.017 - 0.100) g/L. In addition, Product J was tested intact, loose left in, loose filtered through net, loose filtered through sock and loose filtered through 0.45 μ m filter, using the Sea Urchin Fertilization Inhibition Assay. The IC50 of the intact product was 4.79 (4.21 - 5.22) g/L, but the IC50's were <0.12 g/L for the product tested loose left in, or loose filtered (through sock, net, or 0.45 μ m filter).

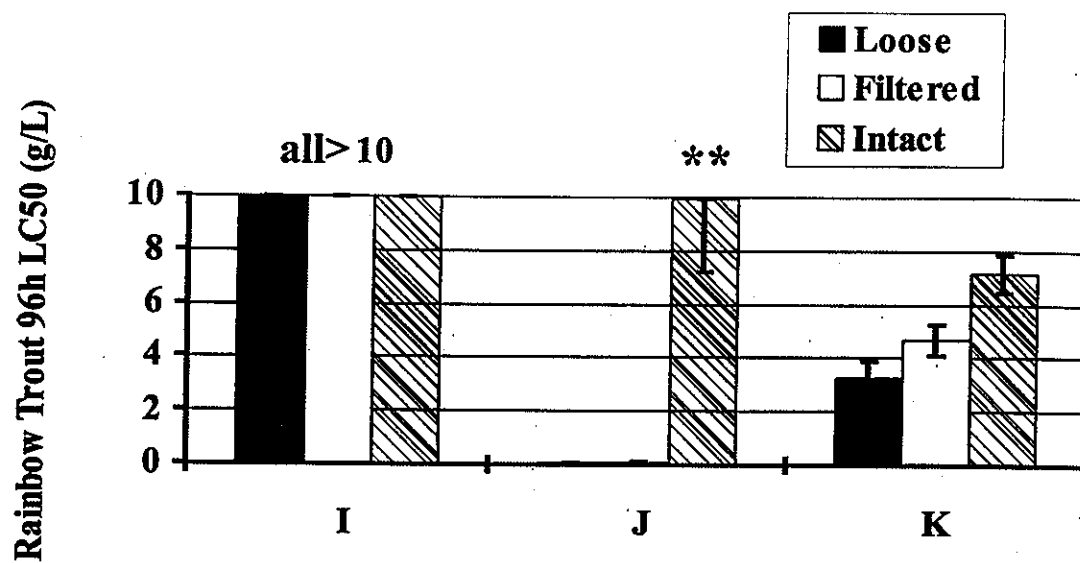


Figure 1 Effect of Handling of Sock-type Sorbents on Rainbow Trout Toxicity Values. (Bars indicate 95% confidence limits; ** = 96h LC50 of 9.92 with an upper limit of 46.0)

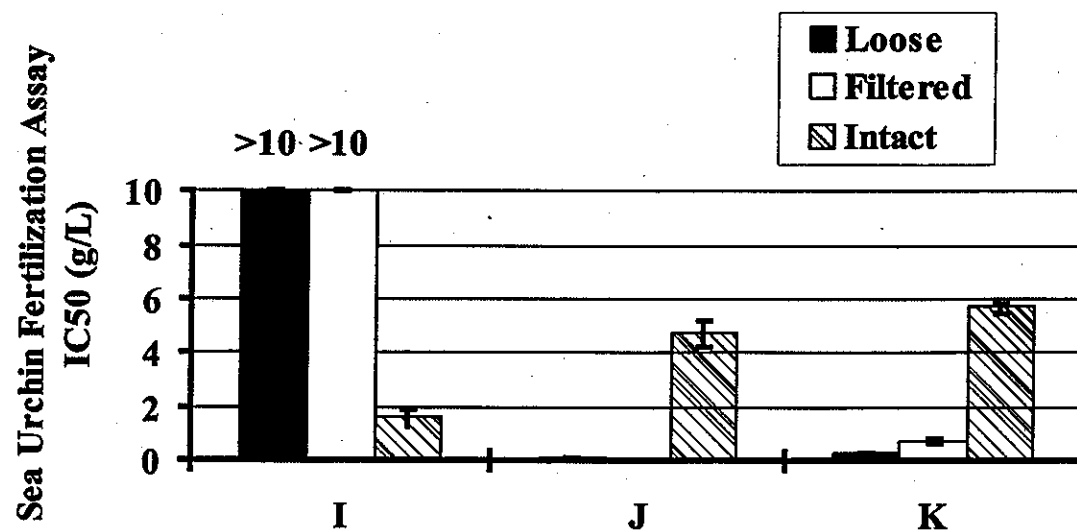


Figure 2 Effect of Handling of Sock-type Sorbents on Sea Urchin Fertilization Inhibition Toxicity Values. (Bars indicate 95% confidence limits)

Product I did not show a difference between handling treatments when tested with the Rainbow Trout Acute Lethality Test (Figure 1). However, when tested with the more sensitive Sea Urchin Fertilization Inhibition Assay, Product I was more toxic when tested intact, indicating that the sock material was toxic (Figure 2). Further testing was performed, and the sock material was found to have a sea urchin fertilization IC₅₀ of 0.234 (0.201 - 0.266) g/L.

4.0 Discussion

The objective of this project was to generate simple test guidelines for screening sorbents for toxicity, and a number of recommendations can be made from our experiments.

Only three species were evaluated to determine how appropriate they were for this use, and two of the three recommended. It is acknowledged that a thorough environmental impact assessment would require a broader range of species.

Sorbents may be in the water for much longer than a day, and there is the potential that some sorbent materials could leach toxicants indefinitely. However, at some point, a sensible soaking cut-off must be chosen. Our data indicate that a minimum 24 hour soaking time is needed to screen sorbents for toxicity, and we recommend that 24 hours be used as the standard.

We debated whether sorbents should be left in the test vessels during the organism exposure period but decided that products should be netted or picked out after soaking, and squeezed to extract water that is returned to the test tank before test animals are exposed. There are several reasons for this. Firstly, the product is intended to be removed from the environment along with the sorbed oil. Secondly, removal lowers the chance of physical damage to the test organisms (e.g. by smothering). Thirdly, some products take up so much water volume that if they are not removed, the test species may die simply due to lack of available water, rather than toxicity of the sorbent.

We tried several different ways of preparing solutions from sock-type sorbents (intact sorbent, loose product filtered through an approximately 0.5 mm mesh size dip net, and loose product filtered through sock material). The effect on toxicity was not consistent. Two of the products were more toxic when tested loose followed by filtration, than they were tested intact. This is most likely due to better water contact and leaching when loose during the soaking period. Since there is the potential for sock-type sorbents to break in the environment, it is recommended that this type of sorbent be soaked loose followed by filtration through an approximately 0.5 mm mesh size dip net, prior to organism introduction. The other test option, filtering loose sorbent product through sock material prior to test species introduction, was not practical, especially for large volume tests such as rainbow trout, which require the filtration of 20 or more litres of solution for each test concentration. It was surprising to find that one of the sock-type products was more toxic when tested intact. This test was repeated with the same result, and the sock material was tested alone and was found toxic. The sock material was toxic rather than the sorbent itself. It is therefore recommended that sock-type sorbents also be tested intact.

The sheet-type sorbent tested in the Species Selection Phase was found to contain an irritating dust when diced, and was the most toxic of the five sorbents tested in the Species Selection Phase. Unfortunately, this product was not available for the intact versus diced sheet comparison performed in the Material Handling Phase. Given that sheet-type products may also break in the environment and release any internal components, we recommend that sheet-type products be diced prior to solution preparation.

The compounds responsible for toxicity were not identified in this study. Some sorbents contain water soluble components which are toxic to the test organisms, as clearly demonstrated by the 0.45 μm filtered solution prepared from Product J. It was also found that one product depressed pH to as low as 3.8 (lethal to rainbow trout).

Now that we have simple test guidelines, a larger number of products should be screened for toxicity, and modelling performed to determine what level of result would indicate that the sorbent material does not contribute significant or meaningful toxicity to the surrounding environment.

5.0 Summary of Toxicity Test Recommendations for Sorbents

1. The maximum sorbent concentration tested should be 10 g/L.
2. Sheet-type sorbents should be cut into 1 cm cubes prior to soaking.
3. Two types of solutions should be prepared from sock-type sorbents and tested. One should be prepared by soaking the intact sorbent (i.e. in sock), and the other should be prepared by soaking the loose sorbent (i.e. minus sock), followed by filtration through a dip net (approx. 0.5 mm mesh size).
4. Sorbents should be soaked for 24 hours to prepare test solutions.
5. Products should be netted or picked out, and squeezed to extract water that is returned to the test tank before test animals are exposed. If the product sinks, it may be left in the tank, unless it interferes with the test animals.
6. The Rainbow Trout Acute Lethality Test (freshwater) and the Sea Urchin Fertilization Inhibition Assay (seawater) are suitable toxicity tests for evaluating sorbents.

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